Temperature dependence of absorption in photorefractive iron-doped lithium niobate crystals

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(Received 28 January 2002; accepted for publication 23 April 2002)

We present experimental data showing a significant dependence of light absorption on temperature in photorefractive $LiNbO_3$:Fe crystals. The results are successfully explained by assuming that the widths of the Fe^{2+} absorption bands in the visible and in the infrared spectral region depend on temperature. The findings are of relevance for thermal fixing of holograms. Furthermore, a temperature-induced increase of the infrared absorption is promising for improved infrared recording. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1486257]

I. INTRODUCTION

Iron-doped photorefractive lithium niobate crystals ($LiNbO_3$:Fe) are recording materials that show potential for, e.g., holographic data storage,[1] holographic wavelength filters,[2] and diffractive optical elements for imaging systems.[3]

Inhomogeneous illumination excites electrons from high intensity areas. They migrate and are trapped in low intensity regions. Thus electric space-charge fields build up and modulate the refractive index via the electro-optic effect. Light absorption is the initial and hence a crucial step of this photorefractive process.[4]

Recording in $LiNbO_3$:Fe at enhanced temperatures (typically 180 °C) yields permanent holograms. This technique is called ''thermal fixing.''[5] The electronic space-charge pattern is copied to an ionic one that is persistent against illumination at room temperature.[6] Although thermal fixing is applied frequently, only little is known about how the electronic excitation and transport parameters are affected by heating.

Holographic recording using near-infrared light is possible in $LiNbO_3$:Fe, but the sensitivity is low.[7] One idea is to increase the infrared absorption by phonon-assisted light-induced excitations. However, according to our knowledge, this effect has not been studied to date.

In this article we examine the effect of temperature on absorption in iron-doped lithium niobate crystals. First we give an outline of the absorption mechanisms. Then we present the experimental methods used and the results obtained. Finally we propose a theoretical model which explains our experimental observations and discuss its implications in terms of possible applications and extensions to different dopants.

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II. ABSORPTION MECHANISMS IN $LiNbO_3$:Fe

The introduction of Fe atoms in $LiNbO_3$ crystals generates two absorption bands (Fig. 1). Absorption of blue or green light excites electrons from Fe^{2+} to the conduction band, generating Fe^{3+}.[8] Furthermore, there is a crystal-field splitting of the Fe^{2+} level, adding a new energy level denoted $(Fe^{2+})^*$.[8] The excitation $Fe^{2+} \rightarrow (Fe^{2+})^*$ takes place at about 1200 nm. In addition, $LiNbO_3$ shows fundamental band-to-band absorption at short wavelengths, starting with a weak tail at about 600 nm, and becoming strong below 400 nm.

The absorption peaks attributed to the abovementioned mechanisms are fairly broad. We assume that thermal vibrations of the crystal lattice induce broadening of the corresponding energy states.[9,10] Two important outcomes of this model are: (1) on the energy scale, absorption spectra should have a Gaussian shape and (2) in the ground state as well as in the excited state the electrons can have vibrational thermal energy that decreases or increases the photon energy required for an optical transition.

III. THEORETICAL CONSIDERATIONS

As mentioned in Sec. II, each absorption band on the α versus E curve should have a Gaussian shape:

$$\alpha = \frac{C}{\sigma} \exp\left[-\left(\frac{E - E_0}{\sigma} \right)^2 \right], \tag{1}$$

where E_0 is the peak absorption energy, σ is the width of the absorption band, and C is a constant proportional to the concentration of atoms responsible for the absorption in that band.

We propose that, for each absorption band, the width σ is an increasing function of temperature T, while the other parameters, E_0 and C, are temperature independent. Therefore the change in absorption $\Delta\alpha$ will follow:

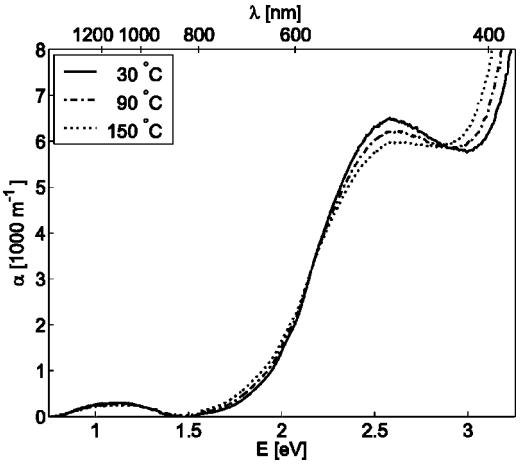

FIG. 1. Absorption coefficient α vs photon energy E with varying crystal temperature. Ordinary light polarization is used.

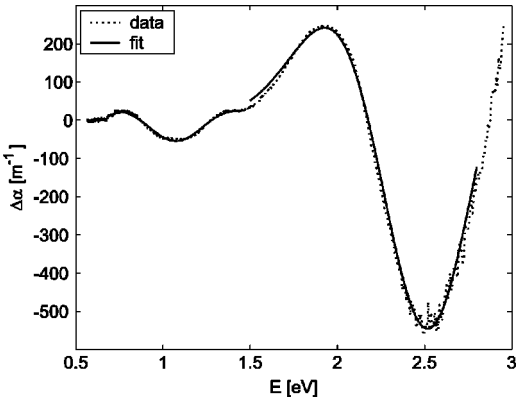

FIG. 2. Absorption coefficient change $\Delta\alpha$ between 30 °C and 150 °C (dotted line) and fitting curves (solid lines). Ordinary light polarization is used.

$$\Delta\alpha = C\left\{\frac{1}{\sigma_1}\exp\left[-\left(\frac{E-E_0}{\sigma_1}\right)^2\right] - \frac{1}{\sigma_2}\exp\left[-\left(\frac{E-E_0}{\sigma_2}\right)^2\right]\right\}, \quad (2)$$

where $\sigma_1=\sigma(T_1)$ and $\sigma_2=\sigma(T_2)$.

IV. EXPERIMENTAL METHODS

We use a Cary 500 spectrometer to measure the optical density of a $LiNbO_3$:Fe crystal. The Fe doping level of our crystal is 5.6×10^{25} atoms/m^3, and the concentration ratio $c_{Fe^{2+}}/c_{Fe^{3+}}$ is 0.32. The dimensions of the crystal are $1.2\times4.9\times5.1$ mm^3, with the c-axis along the longest dimension. Light propagates along the shortest dimension of the crystal. A polarizer is used to select the polarization state of the incident light. We mount the crystal on a custom-made heatable holder, whose temperature we adjust with a Eurotherm 2000 temperature controller, that provides us 0.1 °C accuracy. The holder keeps the crystal tilted to a 5° angle to avoid Fabry–Perot effects.

We vary the temperature of the crystal in the range from 30 to 150 °C with 10 °C steps. For each temperature we measure the optical density. We then proceed to reflection correction taking into account the dependence of the refractive index n on wavelength (modified Sellmeier equations) and on temperature,[11] as well as the thermal expansion of the crystal.[12,13] From this data we calculate the optical absorption coefficient α.

V. EXPERIMENTAL RESULTS

A. Temperature dependence of absorption

Our initial results consist of curves of optical absorption coefficient α versus photon energy E for various temperatures (see, e.g., Fig. 1). In order to obtain a clearer view, as well as to exclude band-edge effects, we proceed to subtract the α versus E curves pairwise. Thus we obtain the curves of $\Delta\alpha=\alpha(T_1)-\alpha(T_2)$ versus E shown in Fig. 2.

We fit the experimentally obtained $\Delta\alpha$ versus E curves to Eq. (2). For each absorption band we isolate the corresponding photon energy region, and feed the data of all absorption differences $\Delta\alpha$ to our fitting algorithm simultaneously. We obtain as fit parameters the absorption width $\sigma(T)$ for all temperatures, as well as C and E_0. A comparison of experimental data and fitting curves can be seen in Fig. 2.

It makes sense to keep the parameter C constant across all temperatures for each absorption band, since it is related to the total number of absorbing atoms that is not changed by heating. And since just a single photorefractive center is involved, the energy position E_0 of the absorption band should also remain constant versus temperature. The resulting values and 95% confidence intervals for E_0 are 2.6264 ± 0.0012, 2.5179 ± 0.0007, and 1.0740 ± 0.0005 eV for extraordinary light polarization at high photon energy, ordinary polarization at high photon energy, and ordinary polarization at low photon energy, respectively.

The resulting fitting parameters for σ, the absorption band width, are shown in Fig. 3 for all three absorption bands. Error bars indicate the 95% confidence intervals. As predicted by our model, the absorption width increases with temperature.

Experimental error in the measurement of the crystal thickness d, the refractive index n, and its optical density OD result in an uncertainty of a few percent for the values of $\Delta\alpha$ used for fitting. The fitting error we obtain is comparable to the experimental uncertainty, providing a strong indication that our theoretical model is an adequate description of the experimental data.

B. Polarization dependence

In Fig. 3 we present fit parameters for different light polarizations and photon energy levels. High photon energy levels (around 2.5 eV) correspond to the $Fe^{2+}\rightarrow Fe^{3+}+e^-$ transition, and low photon energy levels (about 1 eV) to the $Fe^{2+}\rightarrow(Fe^{2+})^*$ transition. No results are presented for extraordinary light polarization and low photon energy, since the $Fe^{2+}\rightarrow(Fe^{2+})^*$ transition is very weak for this light polarization.[8]

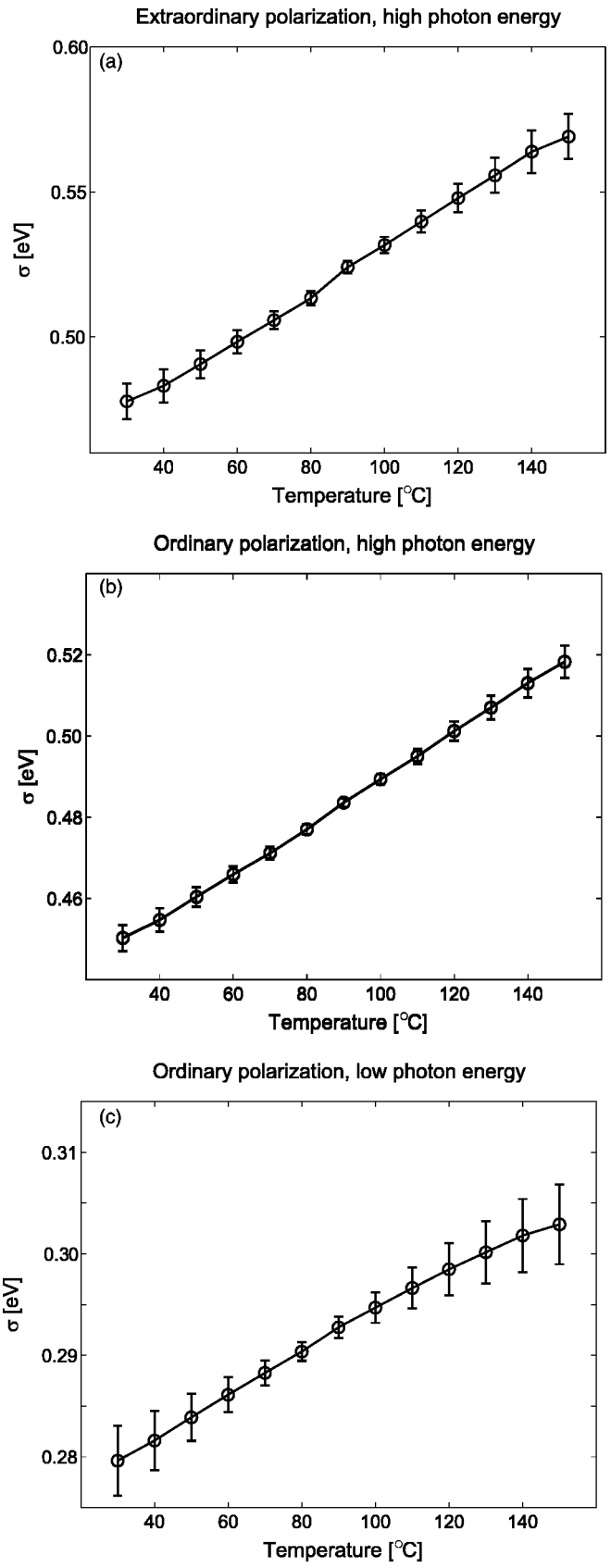

FIG. 3. Absorption widths σ [fit parameters to Eq. (2)] for different light polarization states and photon energy levels. (a) Extraordinary light polarization, high photon energy. (b) Ordinary light polarization, high photon energy. (c) Ordinary light polarization, low photon energy. The connecting lines are guides for the eye.

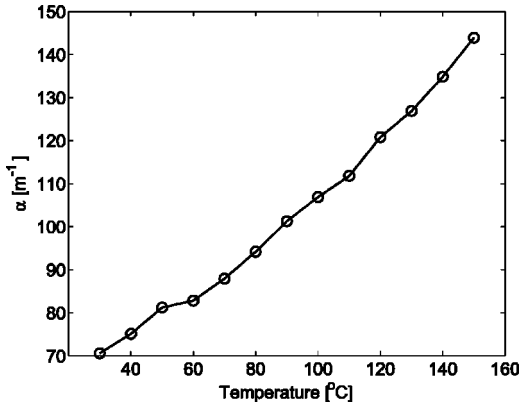

FIG. 4. Absorption coefficient α at 780 nm vs temperature for ordinary light polarization. The connecting line is a guide for the eye.

We notice that the absorption width corresponding to the $Fe^{2+} \rightarrow Fe^{3+} + e^-$ transition $[\sigma(T = 30\,^\circ\mathrm{C}) \simeq 0.46\ \mathrm{eV}]$ is larger than the width corresponding to the $Fe^{2+} \rightarrow (Fe^{2+})^*$ transition $[\sigma(T = 30\,^\circ\mathrm{C}) \simeq 0.28\ \mathrm{eV}]$. For the high photon energy absorption band, the width of the band σ, and its variation versus temperature, depend rather weakly on light polarization. The absorption band for extraordinary light polarization is slightly broader (about 10%) than that for ordinarily polarized light.

C. Absorption increase in the near infrared

In Fig. 4 we show the absorption coefficient α at 780 nm versus temperature T. The data shown in this figure were obtained directly from measurement, using ordinarily polarized light. The absorption coefficient α more than doubles as a result of moderate heating (to 150 °C). This significant increase of absorption is very promising for a corresponding increase in holographic recording sensitivity in the infrared region.

VI. DISCUSSION

The measurements show that the width of each absorption band depends on temperature. Thus our initial assumption, that the line-broadening arises chiefly from thermal processes, is confirmed.

Our experiments reveal that the Fe^{2+} absorption bands in $LiNbO_3$ are significantly broadened (up to about 0.07 eV for ordinary light polarization and 0.09 eV for extraordinary light polarization) by moderate heating (up to 150 °C). The width of the absorption bands increases linearly with temperature both in the visible and infrared regions.

In Eq. (1) the absorption coefficient α due to a specific transition is modeled as a Gaussian whose only temperature dependent parameter is the width σ. The area under the Gaussian function which is proportional to the number of atoms participating in the corresponding transition should remain constant with temperature, as should the photon energy corresponding to maximum absorption.

Our experimental results confirm this theoretical model. Indeed, we obtain good fits of experimental data to Eq. (2), assuming constant values for C and E_0, while σ increases linearly with temperature.

The dependence of absorption on temperature is of great practical importance. Thermal fixing techniques that are widely used to provide holograms with long lifetimes require recording at high temperature. Knowledge of the behavior of absorption at such high temperatures is essential in enabling a better understanding of the mechanisms involved. Our results also indicate that by increasing the temperature of $LiNbO_3$:Fe, spectral sensitivity can be broadened, thus most probably facilitating improved holographic recording in the infrared region.

As we mentioned at the beginning of this section, the physical mechanisms leading to absorption broadening are very fundamental. $LiNbO_3$ crystals with different dopants and even different photorefractive crystals should exhibit similar behaviors. In all these cases temperature tuning of absorption and therefore sensitivity should be possible, enabling holographic recording in parts of the spectrum which are inaccessible at room temperature.

ACKNOWLEDGMENTS

Fruitful discussions with O. F. Schirmer, M. Wöhlecke, and Y. Abu-Mostafa are highly appreciated. Financial support by the NSF and DAAD is gratefully acknowledged.

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